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Some Double Halides of Zinc.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

DANIEL BASE.

1895.

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SOME DOUBLE HALIDES OF ZINC.

INTRODUCTION.

Investigations in the field of double halides have been carried on in this laboratry since 1888, as a result of Prof. Remsen's generalization[1] governing the composition of double halides. This law is based on the study of a large number of facts, namely, more than four hundred compounds. The so-called double compounds, or salts, have been known for a long time, and at different times chemists have called attention to them and offered various explanations of their structure. On account of the difficulty of finding an explanation that did not conflict with the valence theory, chemists were, for the most part, content to pass the double salts by under the name of molecular compounds, a term which carries no more explanation with it then the term gravity does in the case of the falling of bodies to the earth.

The distinction between acidic and basic oxides has long been recognized, having been one of the factors which gave rise to the old dualistic, or electrochemical theory of Berzelius. A similar distinction between acidic and basic halides has also been made, and this was first done by von Bonsdorff,[2] who suggested that double halides were formed by the union of acidic with basic halides, in the same manner in which acid oxides unite with basic oxides to form the so-called true salts. About the same time Boullay[3] called attention to the same distinction and pointed out the similarity between the oxides, sulphides, chlorides, bromides, etc., and designated the compounds formed by the union of acid and basic halogen compounds as true salts, in contradistinction to molecular compounds. These views were held by some other chemists, notably Dr. Hare,[4] of Philadelphia.

Liebig[5] and Berzelius[6] opposed this conception of double halides, and because of their great influence, the views of von Bonsdorff and Boullay were not generally accepted, and the

1 Am. Chem. J., **11**, 291.
2 Ann. chim. phys., **34**, 142.
3 *Ibid*, **34**, 142.
4 Compendium, 1840.
5 Ann. chim. phys., **35**, 68.
6 J., **8**, 138.

close analogy between double halides and oxygen salts was almost completely lost from view.

In 1889, Prof. Remsen, in an extended article, brought forward again the whole subject and showed the close analogy between oxygen salts and halogen double salts, both in composition and the act of formation, and after studying 400 compounds or more, deduced the following generalization:

"When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of alkali salt which are added to one molecule of the other halide, is never greater and is generally less than the number of halogen atoms contained in the latter."

To explain this regularity it was suggested that "two halogen atoms together can play the same part that the so-called linking oxygen atom plays in the oxygen salts," thus,

$$Al\begin{matrix}\diagup O \\ \diagdown OK\end{matrix}, \quad Al\begin{matrix}\diagup Cl_2 \\ \diagdown Cl_2K\end{matrix}, \text{ or } Al.Cl_3.KCl.$$

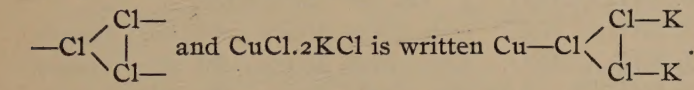
This explanation had been proposed many years before, first by Naquet,[1] in 1861. The same view was held by Blomstrand,[2] Jörgensen,[3] Mallet,[4] Francke,[5] Heyes,[6] and others. Thus this idea of two halogen atoms taking the place of one oxygen atom was not a new one, but it had not hitherto met with general acceptance, chiefly because the evidence in its favor had never been fully presented. The principal objection to this theory, which comes from Horstmann,[7] is suggested by the theory of constant valence and the univalence of the halogen atoms. But as nearly all chemists to-day accept the view of variable valence of the halogens, the objection of Horstmann loses its weight, and it can safely be said that the views of Remsen are pretty generally accepted. The investigations on double halides, that have since been carried out, have for their purpose the testing of the law of composition of these salts, and the verification of the view as to their structure, that two chlorine atoms play the part of a bivalent group and have a linking function.

[1] Principes de chimie fondée sur les théories modernes. Par A Naquet.
[2] Chemie der Jetztzeit.
[3] J. prakt. chem., **16**, 352.
[4] Am. chem. J., **3**, 189.
[5] J. prakt. chem. (N. F.), **36**, 451.
[6] Phil. mag., **25**, 221, 297.
[7] Am. J. Sci., Dec. (1893.)

Over against the 400 compounds, or more, which come under the law, there are a few exceptions which require an extension. The exceptions have been reduced to a small number. The two salts longest known are $CuCl.2KCl$ and $CdCl_2.4KCl$. Recently, Wells and Walden,[1] and Wells and Campbell,[2] have brought out new compounds which cannot be explained under the old form of the law. These are:

$CdBr_2.3CsBr.$	$ZnCl_2.3CsCl.$
$CdI_2.3CsI.$	$ZnBr_2.3CsBr.$
	$ZnI_2.3CsI.$

To explain these an extension of the law has been made, which is, that just as two chlorine atoms can play the part of a bivalent group, so three chlorine atoms together can play the part of a trivalent group. This view is expressed thus,



Some of the salts prepared by me in this investigation fall under this extension of the law. In recent years a new field has been opened in the study of double halides, in that salts have been made containing organic aromatic bases, chiefly aniline and the toluidines, instead of inorganic halides, as one of the constituents of the double salt. Swan, in 1893, and Slagle, in 1894, both working in this laboratory, studied respectively the double salts of mercury and tin with aromatic bases. Their results were in accordance with the law as first put forth.

This is not strictly a new field, for numerous examples of double salts with organic bases have been recorded, but these were not made with a view of bearing out or refuting any principle, such as the theory of double salts, and in no case was a thorough study made, the only object being to get a salt of the organic halide with an inorganic one for the sake of better characterizing the organic compound.

To continue the investigation of double halides containing organic bases, it seemed desirable to study the double salts of zinc with aniline and the toluidines, an account of which is

[1] Am. J. Sci., Dec. [1893]. [2] *Ibid.*

given in this paper. As the halides of the organic bases are closely related to the ammonium halides, and as a number of zinc ammonium double chlorides are recorded in the literature, some of which do not conform to the law and the authority for which might be questioned, it seemed proper, at the same time, to make a study of these compounds. This work will be spoken of in the latter part of this paper.

All the double salts of zinc with inorganic as well as organic halides, that have been recorded in the Jahresberichte up to the year 1888 inclusive, and in the other journals up to the present, have been collected and tabulated. For the sake of completeness, it was thought well to give these salts with the references.

Double Chlorides.

$ZnCl_2.2NH_4Cl.H_2O$. J., **12**, 148; Schindler.

$ZnCl_2.2NH_4Cl.H_2O$. Ann. chem. pharm., **66**, 280; Hautz.

$ZnCl_2.NH_4Cl.2H_2O$. Ann. chem. pharm., **66**, 280; Hautz.

$ZnCl_2.2NH_4Cl$. Ann. der Phys. Pogg., **94**, 507; Rammelsberg.

$ZnCl_2.NH_4Cl$. Ann. des Mines (5), **12**, 1; Marignac.

$ZnCl_2.3NH_4Cl$. Ann. des Mines (5), **12**, 1; Marignac.

$ZnCl_2.3NH_4Cl.H_2O$. Ann. chim. phys. Berthelot and André.

$ZnCl_2.6NH_4Cl\frac{2}{3}H_2O$. Ann. chim. phys. Berthelot and André.

$ZnCl_24NH_4Cl$. Bl. (1861), 51; Dehérain.

$ZnCl_2.2KCl$. Ann. der phys. Pogg., **94**, 507; Rammelsberg.

$ZnCl_2.2HCl$. Ann. des Mines [5], **12**, 1; Marignac.

$ZnCl_2.2NaCl.3H_2O$. Ann. des Mines [5], **12**, 1; Marignac.

$ZnCl_2BaCl_2.4H_2O$. J. (1873), 273; G. Werner.

$ZnCl_2MgCl_2.6H_2O$. J. (1873), 273; G. Werner.

$ZnCl_2.3CsCl$. Am. J. Sci., Dec. 1893; Wells and Campbell.

$ZnCl_2.2CsCl$. Am. J. Sci., Dec. 1893; Wells and Campbell.

$ZnCl_2.PtCl_2.6H_2O$. J. (1877), 312; Nilson

$ZnCl_2.PtCl_4.6H_2O$. J. (1870), 393; Topsoë.

$ZnCl_2.PdCl_46H_2O$. J. (1870), 393; Topsoë.

$ZnCl_2.2(AuCl_3).8H_2O$. J. (1874), 177; Topsoë.

$ZnCl_2.2(AuCl_3).12H_2O$. Ann. der phys. Pogg., **17**, 261; **33**, 64; Bonsdorff.

$ZnCl_2.2AuCl_3$. Ann. der phys. Pogg., **17,** 261; **33,** 64; Bonsdorff.

Double Chlorides with Organic Constituent.

$ZnCl_2.2(C_9H_4N_2.HCl.$Cyanconiïne). J. prakt. chem. [2], **22,** 26; E. v. Meyer.

$ZnCl_2.2(C_9H_7N.HCl.$Quinoline). Ber. d. chem. Ges., (1882), 645; Wallack.

$ZnCl_2.2($Tetraethyldiamidotriphenylcarbinol.2HCl). J. (1883), 695; Döbner.

$ZnCl_2.$(*p*-amido-*o*-imido-phenylurea). Ber. d. chem. Ges., (1884), 2625; Hager.

$ZnCl_2.$(Quinine.2HCl).$2H_2O$. J. (885), .1707; Comstock and Königs.

$ZnCl_2.2$(papaverin.HCl). J. (1885), 1697; Goldschmidt.

$ZnCl_2.$(*β*-picolin.HCl). Ber. d. chem. Ges., (1885), 3091; Ad. Hesekiel.

$ZnCl_2.2$(*α*-*γ*-dimethylquinoline.HCl). J. (1886), 935; C. Beyer.

$ZnI_2.2$(papaverin.HCl). J. (1886), 1716; Jahoda.

$ZnCl_2.2$(Ethyltriamidonaphthalin.HCl). J. Chem. Soc.; Meldola and Streatfield.

$ZnCl_2.$(isocinchonine.2HCl). Ber. d. chem. Ges. (1888), 2510; Comstock and Königs.

$ZnCl_2.2(C_5H_6N.HCl)$. Ber. d. chem. Ges. (1888), 1578; Lang.

$ZnCl_2.$(dipyridin.2HCl). J. Chem. Soc. [2], **7,** 406; Anderson.

Double Bromides.

$ZnBr_2 2CsBr$. Am. J. Sci., Dec. 1893; Wells and Campbell.

$ZnBr_2 3CsBr$. Am. J. Sci., Dec. 1893; Wells and Campbell.

$ZnBr_2 2NH_4Br$. J. (1860), 17.

$3ZnBr_2 2DiBr_3.36H_2O$. J. (1878), 245: Frerichs and Smith

$3ZnBr_2 DiBr_3.12H_2O$. J. (1885), 481; P. T. Cleve.

$3ZnBr_2.2LaBr_3.39H_2O$. Ann chem. (Liebig), **191,** 331.

$ZnBr_2.PtBr_4.12H_2O$. J. (1868), 274; Topsoë.

Double Iodides.

$ZnI_2.2NH_4I$. J., **19,** 256; Rammelsberg.

$ZnI_2.KI$. J., **19,** 256; Rammelsberg.
$ZnI_2.2NaI.3H_2O$. J., **19,** 256; Rammelsberg.
$2ZnI_2BaI_2$. J., **19,** 256. Rammelsberg.
$ZnI.As(CH_3)_4I$ (old formula). J. (1859), 431; Cahours.
$ZnI.As(C_2H_5)_4I$ (old formula). J. (1859), 431; Cahours.
$ZnI.P(C_2H_5)_4I$ (old formula). J. (1861), 557; Cahours.
$ZnI.P(C_2H_5)3HI$ old formula.) J. (1861), 557; Cahours.
$ZnI.BiI_3.12HO$ (old formula).
$3ZnI_2.2DiI_3.24H_2O$. J. (1878), 245; Frerichs and Smith.
$3ZnI_2.2LaI_3.27H_2O$. J. (1878), 245; Frerichs and Smith.
$ZnI_2.PtI_4.9H_2O$. J. (1870), 389; Topsoë.
$ZnI_2.2CsI$. Am. J. Sic., Dec. 1893; Wells and Walden.
$ZnI_2.3CsI$. Am. J. Sci., Dec. 1893; Wells and Walden.

Double Fluorides.

$ZnFl.SiFl_2.6HO$ (old formula). J. (1859), 108; Marignac.
$ZnFl_2.TaFl_5.7H_2O$. J. (1866), 204; Marignac.
$ZnFl_2.SnFl_4.6H_2O$. J. (1859), 112; Marignac.
$ZnFl_2.2KFl$. Ann. der. phys. Pogg., **1,** 26; Berzelius.
$ZnFl_2.Al_2Fl_6$. Ann. der. phys. Pogg., **1,** 26; Berzelius.
$ZnFl_2.KFl$. B. (1886), 896; Wagner.
$ZnFl_2.NaFl$. B. (1886), 896; Wagner.
$ZnFl_2.2NH_4Fl.2H_2O$. B. (1886), 896; Wagner.
$ZnFl_2.2BFl_3$. Ber. d. chem. Ges. (1886), 896; Wagner.
$2ZnFl_2.Mn_2Fl_6.8H_2O$. J. (1886), 420; Christensen.

It will be seen that some of the compounds recorded above do not come under the law of the composition of double halides, or the extension of the law. However, it would be necessary to repeat the work before accepting these few exceptions as speaking against the law. One of the ammonium zinc double chlorides recorded is apparently an exception, but by repeating the work it was possible to obtain only two double ammonium salts, both of which fall under the law or its extension.

The meterials used were prepared in the usual way. Zinc chloride and bromide were made by dissolving zinc in the respective acids. Ammonium chloride was sublimed.

Method of Analysis.—The salts were analyzed for zinc, halogen, and water of crystallization when present. Zinc was

precipitated as carbonate and weighed as oxide. The organic bases had no solvent action on the zinc carbonate, as ammonia has when present in the solution.

Chlorine was determined gravimetrically or volumetrically by Volhard's method.

Compounds Described.

$ZnCl_2.2C_6H_5.NH_3.Cl.H_2O$. Dianiline chlorozincate.

$ZnCl_2.3C_6H_5.NH_3.Cl.2H_2O$. Trianiline chlorozincate.

o-$ZnCl_2.2C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}.2H_2O$. Diorthotoluidine chlorozincate.

m-$ZnCl_2.2C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}$. Dimetatoluidine chlorozincate.

m-$ZnCl_2.3C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}$. Trimetatoluidine chlorozincate.

p-$ZnCl_2.2C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}$. Diparatoluidine chlorozincate.

p-$ZnCl_2.3C_6H_4\begin{matrix}CH_3\\NH_3Cl\end{matrix}$. Triparatoluidine chlorozincate.

$ZnBr_2.2C_6H_5NH_3BrH_2O$. Dianiline bromozincate.

o-$ZnBr_2.2C_6H_4\begin{matrix}CH_2.H_2O\\NH_3Br\end{matrix}$. Diorthotoluidine bromozincate.

m-$ZnBr_2.2C_6H_4\begin{matrix}CH_3\\NH_3Br.2H_2O\end{matrix}$. Dimetatoluidine bromozincate.

m-$ZnBr_2.3C_6H_4\begin{matrix}CH_3\\NH_3Br\end{matrix}$. Trimetaloluidine bromozincate.

p-$ZnBr_2.2C_6H_4\begin{matrix}CH_3\\NH_3BrH_2O\end{matrix}$. Diparatoluidine bromozincate.

$ZnCl_2.2NH_4Cl$. Diammonium chlorozincate.

$ZnCl_2.3NH_4Cl$. Triammonium chlorozincate.

DOUBLE CHLORIDES.

Dianiline chlorozincate, $ZnCl_2.2C_6H_5NH_3Cl.H_2O$.—This salt was made by H. Vohl,[1] in 1865, in an indirect way. In an article, "On the compounds of zinc chloride with aniline and the application of the same in the arts," Vohl describes the preparation of the salt $ZnCl_2.2C_6H_5NH_2$. It forms, according

[1] Ding. pol. j., **175**, 211.

to him, shining white needles, decomposed by water and obtained from alcohol. In dilute hydrochloric acid the compound is easily soluble and yields a salt crystallizing in large colorless columnar crystals and plates, which become colored to a violet blue in contact with the air. This salt is easily soluble in alcohol and water. It contains water of crystallization which escapes completely at 105° C. Heated more strongly it melts, vapors of aniline hydrochloride are formed while zinc chloride remains behind, which takes on a violet blue color.

This description of the double salt by Vohl was found to be correct, and his analyses were good, showing the salt to have the above formula. His object in making the double salts was to prepare aniline dyes in accordance with the method in use at that time. By mixing the double salt with an oxidizing agent, as mercurous nitrate, and heating, fuchsine was formed. Vohl made no systematic study of double salts nor had he any idea of getting more than one aniline salt, and therefore a repetition of the work in a thorough manner was necessary, especially as the object now is to get evidence for or against the law of composition of double salts. My work has shown that there are two double aniline salts, one being identical with that described by Vohl.

When zinc chloride and aniline hydrochloride are mixed so that the number of molecules of the former to those of the latter bear these relations, 3 : 1, 2 : 1, 1 : 1, 1 : 2, dianiline chlorozincate is formed in every case. It seems to make no difference whether the solutions are heated or not, or whether they are neutral or made acid. The solutions soon change color to a reddish brown, or greenish color, even when mixed in the cold. The ease with which they become colored varies with the proportion of aniline hydrochloride present. Alcoholic solutions color extremely rapidly. On standing, a flocculent greenish material is formed in the solutions. The shape of the crystals varies with conditions. The most frequent form is the plates spoken of by Vohl, which belong to the triclinic system. The salt is easily purified by recrystallization from water. When pure it does not change color readily in the air. It loses all its water in the sulphuric acid

desiccator, the weight remaining constant after transferring to an air-bath and heating to 100° centigrade. It is extremely soluble in methyl alcohol, so much so that it cannot be recrystallized from this. It is less soluble in ethyl alcohol.

0.459 gram salt gave 0.0904 gram ZnO and 0.6365 gram AgCl.

0.3912 gram salt gave 0.0772 gram ZnO and 0.5408 gram AgCl.

0.4405 gram salt lost 0.0191 gram water.

	Calculated for $ZnCl_2.2C_6H_5NH_3Cl.H_2O$.	Found. I.	II.	III.
Zn	15.77	15.81	15.82	....
Cl	34.32	34.3	34.18	....
H_2O	4.35	....	....	4.34

Trianiline Chlorozincate, $ZnCl_2.3C_6H_5NH_3Cl.2H_2O$.—When zinc chloride and aniline hydrochloride are brought together in water solution so that the molecular proportions of the former to the latter are as 1 : 3, 1 : 4, 1 : 6, trianiline chlorozincate is formed. The 1 : 3 mixture yields the dianiline salt also, which can easily be separated from the trianiline salt on account of its totally different form. The solutions soon became deeply colored, but the crystals are colored only a little, and by washing with water are good enough for analysis. When pure they are colorless. The salt is more soluble in water and alcohol than the dianiline salt. It is stable in the air but on long exposure it changes color to a green. It loses all its water in the sulphuric acid desiccator, and can be heated in the air-bath to 100° without decomposition. It forms long prisms apparently of the orthorhombic system. The prism forms are unit prism and macro prism.

0.3538 gram salt gave 0.051 gram ZnO and 0.4536 gram AgCl.

0.2875 gram salt gave 0.042 gram ZnO and 0.369 gram AgCl.

0.2194 gram salt lost 0.0143 gram H_2O.

	Calculated for $ZnCl_2.3C_6H_5NH_3Cl.2H_2O$.	Found. I.	II.	III.
Zn	11.62	11.57	11.74	....
Cl	31.58	31.7	31.75	....
H_2O	6.41	....	....	6.52

Diorthotoluidine Chlorozincate, $ZnCl_2.2C_6H_4\begin{matrix}CH_3.H_2O\\NH_3Cl\end{matrix}$.—This compound was prepared in 1865 by Gräfinghoff,[1] who made a study of the action of the toluidines (ortho and para) on zinc chloride. He was led to this study by the work of Vohl, already referred to. His object was the same as Vohl's, that is the preparation of compounds of zinc chloride with toluidine for technical application in the preparation of dyes. On treating the toluidine compound with hydrochloric acid, drying on the water-bath, and taking up with alcohol, he says he obtained the salt $ZnCl.2(C_7H_9N.HCl)$. This salt, he says, can also be prepared directly from zinc chloride and toluidine hydrochloride, and when obtained from water solution contains water of crystallization, but when obtained from alcohol it contains no water. He says further, "to avoid the objection that the existence of these salts was shown only for the liquid toluidine, toluidine was prepared from pure toluene from tolu balsam, which according to Muspratt and Hofmann, was solid. Salts were formed in the same manner and analyzed, and their identity with those from the liquid toluidine shown. They agreed in solubility and physical properties perfectly with the latter."

Gräfinghoff's object evidently was not to make a systematic study of double halides.

Bibanow[2] also says he obtained from a mixture of orthotoluidine hydrochloride and a concentrated solution of zinc chloride, by cooling down to —5° a salt of the composition $ZnCl_2.2C_6H_4\begin{matrix}CH_3\\NH_3Cl,\end{matrix}$ having no water of crystallization and forming colorless concentrically grouped plates.

Zinc chloride and orthotoluidine hydrochloride were brought together in aqueous solution in the molecular proportions 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4. In the last case the toluidine hydrochloride separated out first. The solutions were heated to boiling and it mattered not whether they were made acid or not. They did not change color nearly so rapidly as the aniline-zinc-hydrochloride solutions, and deposited very little of the green flocculent material.

[1] J. prakt. chem. (1865), **95**, 221. [2] Mon. scient. (3), **4**, 925.

Only one salt was obtained from all these mixtures, as was shown by analysis, the same as was obtained by Grafinghoff. The salt is colorless when pure, but gradually becomes colored when exposed to the air. It gives off water and takes it up again, according to the temperature and hygroscopic state of the atmosphere. Solutions of the salt easily become supersaturated, and, in strong solutions, the salt crystallizes out in long, concentrically grouped plates, as described by Bibanow. The plates are striated, so that they have a sort of hour-glass appearance. They lose all their water over sulphuric acid, and can be heated in the air-bath to 120° without decomposing. When heated high enough, the salt melts to a brown liquid from which toluidine hydrochloride sublimes. As the salt loses water easily, it must be pressed between filter-paper, powdered, and not allowed to lie long in the air before analysis.

0.2775 gram salt lost 0.0024 gram water.

0.2021 gram salt gave 0.0359 gram ZnO and 0.2539 gram AgCl.

0.331 gram salt gave 0.0595 gram ZnO and 0.4171 gram AgCl.

	Calculated for $ZnCl_2.2C_6H_4<^{CH_3.2H_2O}_{NH_3Cl}$.	Found. I.	II.	III.
Zn	14.42	....	14.26	14.33
Cl	30.86	....	31.06	31.16
H_2O	7.83	8.07	....	....

Dimetatoluidine chlorozincate, $ZnCl_2.2C_6H_4<^{CH_3}_{NH_3Cl}$.—This salt is formed when the constituents are brought together in the molecular proportions 3 : 1, 2 : 1. It forms fine, silken needles, which are extremely soluble in water. They cannot be washed, but must be sucked dry on the filter-pump and pressed between filter-paper. Owing to the nature of the crystals and their great solubility, it is very difficult to get a specimen of the salt pure so as to give sharp analyses. The results are not as good as could be desired, but they are close enough to show that the compound has the formula given above.

0.0941 gram salt gave 0.0187 gram ZnO and 0.03187 gram Cl.

0.1917 gram salt gave 0.0377 gram ZnO and 0.2568 gram AgCl.

	Calculated for $ZnCl_2.2C_6H_4<^{CH_3}_{NH_3Cl}$	Found. I.	Found. II.
Zn	15.42	15.95	15.8
Cl	33.48	33.87	33.13

These results were from different specimens.

Trimetatoluidine Chlorozincate, $ZnCl_2.3C_6H_4<^{CH_3}_{NH_3Cl}$.—Mixtures of zinc chloride and metatoluidine hydrochloride were made in aqueous solution in the proportions of 1 : 1, 1 : 2, 1 : 3, 1 : 4. All these gave the same double salt, the trimetatoluidine chlorozincate. The solutions soon assume a purple color, and the crystals are nearly always colored. When pure, they are colorless. The salt crystallizes in fine needles, which grow in radiating tufts and are not as soluble as the ditoluidine salts, but still are too soluble to be washed with water, and must be sucked dry and pressed between drying paper. In this way they are obtained in good condition for analysis.

0.1394 gram salt gave 0.0201 gram ZnO and 0.1751 gram AgCl.

0.1929 gram salt gave 0.028 gram ZnO and 0.2426 gram AgCl.

0.2225 gram salt gave 0.0316 gram ZnO and 0.278 gram AgCl.

	Calculated for $ZnCl_2.3C_6H_4<^{CH_3}_{NH_3Cl}$	Found. I	Found. II	Found. III
Zn	11.5	11.57	11.65	11.4
Cl	31.24	31.06	31.14	30.92

Diparatoluidine Chlorozincate, $ZnCl_2.2C_6H_4{}^{CH_3}_{NH_3Cl}$.—This salt was referred to under the corresponding orthotoluidine salt. Gräfinghoff said he prepared this at the same time that he made the ortho salt. He did not give any analyses nor did he state whether only one salt could be formed or more than one. There are two para salts, while only one ortho salt could be made.

Diparatoluidine chlorozincate is formed when zinc chloride and toluidine hydrochloride are mixed in the proportions 3 : 1,

2:1, 1:1, 1:2, 1:3. The solutions were heated to boiling and made slightly acid. The salt crystallizes in colorless plates, which form a matted mass.

The solutions color very slowly. They cannot be purified by boiling with boneblack as they become colored more, to a deep purple. The crystals have various forms, sometimes triangular plates, sometimes triangular plates with the angles truncated.

The salt is easily soluble in cold water. It is stable in the air, and does not change color.

0.2567 gram salt gave 0.0489 gram ZnO and 0.3482 gram AgCl.

0.2743 gram salt gave 0.0524 gram ZnO and 0.3709 gram AgCl.

	Calculated for $ZnCl_2.2C_6H_4<^{CH_3}_{NH_3Cl}$.	Found. I.	II.
Zn	15.42	15.3	15.37
Cl	33.48	33.54	33.44

Triparatoluidine Chlorozincate, $ZnCl_2.3C_6H_4{<}^{CH_3}_{NH_3Cl}$.—This salt is formed when zinc chloride and paratoluidine hydrochloride are brought together in water solutions in the proportions 1:3, 1:4. The 1:4 mixture deposits the organic halide first. Sometimes the ditoluidine salt is formed in the 1:3 mixture. There is this tendency at low temperatures. At a slightly elevated temperature only the 1:3 salt is formed.

The compound crystallizes well, apparently in the triclinic system, and resembles albite crystals in outline. The forms are oP, $\bar{P}'\infty$, $\infty_1'P$, $\infty_1'P$, $\breve{\infty}P\infty$.

0.191 gram salt gave 0.0263 gram ZnO and 0.2406 gram AgCl.

0.2483 gram salt gave 0.0354 gram ZnO and 0.315 gram AgCl.

	Calculated for $ZnCl_2.3C_6H_4<^{CH_3}_{NH_3Cl}$.	Found. I.	II.
Zn	11.50	11.05	11.45
Cl	31.24	31.15	31.37

Double Bromides.

Dianiline Bromozincate, $ZnBr_2.2C_6H_5NH_3Br.H_2O$.—Aniline hydrobromide behaves a little differently from the corresponding chloride, in that it separates out as such from mixtures in which the proportion of aniline hydrobromide to zinc bromide is greater than 2 : 1. A 3 : 1 mixture could not be made as in the case of the chloride. Addition of hydrobromic acid caused a still greater separation of the organic halide. Only one double salt could be obtained from all the different mixtures. It seemed to be best formed in a 1 : 1 solution. Sometimes a solution of one molecule of zinc bromide to two molecules of organic halide would deposit the organic halide along with the double salt. The salt crystallizes in thick prismatic plates resembling those of the corresponding double chloride, and probably belonging to the same system.

The solutions remain colorless, differing again in this respect from those of the corresponding chloride. The salt cannot be recrystallized from water, as aniline hydrobromide separates out. It is easily soluble in cold water. It loses its water on heating and does not decompose at 110°.

0.2452 gram salt gave 0.0345 gram ZnO and 0.3112 gram AgBr.

0.2249 gram salt gave 0.0318 gram ZnO.

0.2609 gram salt gave 0.3315 gram AgBr.

0.1758 gram salt lost 0.0052 in water.

	Calculated for $ZnBr_2.2C_6H_5NH_3Br.H_2O$.	Found. I.	II.	III.	IV.
Zn	11.02	11.30	11.35	....	....
Br	54.19	54.00	....	54.06	....
H_2O	3.05	....	....	....	3.24

Diorthotoluidine Bromozincate, $ZnBr_2 2C_6H_4 \begin{matrix} CH_3.H_2O \\ NH_3Br \end{matrix}$.—Orthotoluidine hydrobromide is like the chloride in its behavior towards zinc bromide, that is, it does not separate out as such from mixtures in which it is present in excess, as the aniline hydrobromide does. Mixtures were made in many proportions, but only one salt could be obtained. The solutions color slowly. The salt forms large colorless prismatic plates, which can be recrystallized from water. It can be

heated in the air-bath to 120° without decomposition, and when heated to 150° it begins to melt to a blue liquid, giving off vapors of toluidine hydrobromide. The salt is readily soluble in cold water.

0.2564 gram salt gave 0.0339 gram ZnO and 0.31 gram AgBr.

0.6305 gram salt gave 0.852 gram ZnO and 0.7963 gram AgBr.

0.3802 gram salt lost 0.0117 gram water.

	Calculated for $ZnBr_2.2C_6H_4<^{CH_3.H_2O}_{NH_3Br}$.	Found. I.	II.	III.
Zn	10.52	10.56	10.82	....
Br	51.7	51.45	51.82	....
H_2O	2.9	....	....	3.08

Dimetatoluidine bromozincate, $ZnBr_2.2C_6H_4<^{CH_3.2H_2O}_{NH_3Br}$.— This salt is formed in solutions which contain zinc bromide in excess, that is, in 3 : 1, 2 : 1, 1 : 1, solutions. The salt is with difficulty obtained in pure condition, as there is a strong tendency to the formation of a tritoluidine salt, to be described presently.

Sometimes in these mixtures one crop will be the ditoluidine salt, the next crop a tritoluidine salt, and the third a ditoluidine salt again. The ditoluidine salt forms long thick prismatic bars. The solution soon becomes colored and the crystals are nearly always more or less colored.

The compound loses its water in the air-bath and can be heated above 100° without decomposing.

0.2647 gram salt gave 0.0336 gram ZnO and 0.3128 gram AgBr.

0.2184 gram salt gave 0.0275 gram ZnO and 0.2581 gram AgBr.

0.2647 gram salt lost 0.0148 gram water.

	Calculated for $ZnBr_2.2C_6H_4<^{CH_3.2H_2O}_{NH_3Br}$.	Found. I.	II.	III.
Zn	10.23	10.28	10.11	....
Br	50.20	50.27	50.28	....
H_2O	5.64	....	....	5.59

Trimetatoluidine Bromozincate, $ZnBr.3C_6H_4\begin{matrix}CH_3\\NH_3Br\end{matrix}$. — Of the two metatoluidine double salts this one is most easily formed, being produced in solutions containing an excess of zinc bromide as well as in those in which the toluidine hydrobromide is in excess. It crystallizes in long needles or prisms, for the most part colored purple. By pressing between filter-paper they are fit for analysis.

0.2291 gram salt gave 0.0237 gram ZnO and 0.11575 gram Br.

0.2663 gram salt gave 0.0289 gram ZnO and 0.1346 gram Br.

	Calculated for $ZnBr_2.3C_6H_4<\begin{matrix}CH_3\\CH_3Br\end{matrix}$.	Found. I.	II.
Zn	8.26	8.30	8.47
Br	50.71	50.52	50.54

These salts are much less soluble in cold water than the corresponding chlorine salt. It was impossible to wash the latter without dissolving the crop of crystals, while the former can be washed clean on the filter-pump.

Diparatoluidine Bromozincate, $ZnBr_2.2C_6H_4\begin{matrix}CH_3\\NH_3Br\end{matrix}$.—When solutions of zinc bromide and paratoluidine hydrobromide are made in the proportions of 1 : 1, 1 : 2, 1 : 3, the paratoluidine hydrobromide crystallizes out without forming a double salt. Addition of hydrobromic acid causes more of the organic halide to separate out. In this respect, the behavior is like that of aniline hydrobromide. Mixtures containing zinc bromide in excess, for example 2 : 1, 3 : 1, yield a double salt, crystallizing in large thin shining colorless leaves. These were filtered off, sucked dry, and pressed between filter-paper. When washed with water the crystals become opaque at once, evidently being decomposed. On trying to recrystallize the salt from water, it is broken down, yielding crystals of paratoluidine hydrobromide. The salt is stable in the air and does not change color.

0.2122 gram salt gave 0.0283 gram ZnO.

0.1495 gram salt gave 0.1826 gram AgBr.

0.255 gram salt gave 0.0345 gram ZnO and 0.3107 gram AgBr.

0.2302 gram salt lost 0.0072 gram water.

	Calculated for $ZnBr_2.2C_6H_4<^{CH_2.H_2O}_{NH_3Br}$.	Found. I.	II.	III.	IV.
Zn	10.52	10.71	....	10.85	....
Br	51.70	....	51.97	51.84	....
H_2O	2.9	....	....	....	3.12

Double Ammonium Zinc Chlorides.

As was stated in the beginning of this paper, the close relationship between ammonia and the organic bases made it desirable to investigate the double zinc ammonium chlorides, along with those of the organic bases, especially since a number of them are recorded, in regard to some of which a doubt may arise as to their existence. The following salts are recorded:

1. $ZnCl_2.2NH_4Cl.H_2O$. Schindler, J. **12,** 148; Hautz, Ann. Chem. (Liebig), **66,** 287. The latter says he obtained the salt from one part ammonium chloride and two parts zinc chloride.

2. $ZnCl_2.NH_4Cl.2H_2O$. Hautz, *loc. cit.* He mixed one part of each constituent and obtained this salt in large shining leaves, as he says.

3. $ZnCl_2.2NH_4Cl$. Rammelsberg. Ann. der phys. (Pogg.) **94,** 507; also Marignac, Ann. des Mines [5] **12,** 1.

4. $ZnCl_2.3NH_4Cl$. Marignac, *loc. cit.*

5. $ZnCl_2.NH_4Cl$. } Dehérain, Bl. (1861), 51; says that
6. $ZnCl_2.4NH_4Cl$. } $ZnCl_2.NH_4$, $ZnCl_2.2NH_4$, and $ZnCl_2.NH_4$, when dissolved in hydrochloric acid, yield corresponding double chlorides.

7. $ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O$. } Berthelot and André, Ann.
8. $ZnCl_2.3NN_4Cl.H_2O$. } chim. phys. (6), **11,** 294–310. These chemists mention the existence of these two salts but do not state how they were obtained.

By working under various conditions, I was able to obtain only two double salts, *viz.*, Nos. 3 and 4 in the list above, which were also obtained by Marignac. He did not make a thorough study, but made a mixture in only one molecular proportion. As these salts were completely described by Ma-

rignac, I cannot do better than to give his own words. He says, "In his treatise on crystallographical chemistry, Rammelsberg describes the crystal forms of this salt, *i. e.*, No. 3, to which he attributes the formula $ZnCl_2.2NH_4Cl$. An earlier analysis by Schindler made it appear to contain an equivalent of water. And it is to be noticed that the crystals described by Rammelsberg may be regarded as isomorphous with the stannous ammonium chloride described by the same chemist, of which he represents the composition by the formula $SnCl_2.2NH_4Cl.H_2O$. These considerations have induced me to undertake again the examination of these salts. The results have not answered to what I supposed, but they are not the less curious. They prove, in effect, the existence of two double salts, both anhydrous, and represented by the formulas (see 3 and 4 above). What is most singular is that these two salts, perfectly distinct as regards their appearance and their faces, have forms which can be derived from one another. However, one cannot call them isomorphous, since they do not mix in anywise in crystallizing, and there is no passage from the one to the other, although they are formed sometimes simultaneously in the same beaker."

Marignac calls $ZnCl_2.2NH_4Cl$ the laminated salt and $ZnCl_2.3NH_4Cl$ the prismatic salt. He dried the salts in all cases at 100°, at which temperature they preserved their transparency and lost only a trace of hygroscopic water. The prismatic crystals are right rhombohedral prisms.

Diammonium chlorozincate, $ZnCl_2.2NH_4Cl$.—Mixtures of zinc chloride and ammonium chloride were made in the molecular proportions of 3 : 1, 2 : 1, 1 : 1, 1 : 2. The same salt was obtained from all of them, the laminated salt of Marignac. It forms large shining plates. Sometimes a 1 : 2 mixture gave the 1 : 3 salt at first, and the 1 : 2 salt in later crops. The mixtures were neutral or slightly acid.

0.2125 gram salt gave 0.0711 gram ZnO and 0.5036 gram AgCl.

0.1891 gram salt gave 0.0632 gram ZnO.

0.2456 gram salt gave 0.5776 gram AgCl.

	Calculated for $ZnCl_2.2NH_4Cl$.	Found. I.	II.	III.
Zn	26.83	26.86	26.84	....
Cl	58.32	58.60	....	58.16

Triammonium Chlorozincate, $ZnCl_2.3NH_4Cl$.—Solutions of zinc chloride and ammonium chloride, in the proportions of 1:3, 1:4, 1:6, gave only the 1:3 salt. In the 1:6 solution, ammonium chloride crystallized out first.

0.1546 gram salt gave 0.0424 gram ZnO and 0.3759 gram AgCl.

0.4685 gram salt gave 0.1272 gram ZnO and 1.1267 grams AgCl.

	Calculated for $ZnCl_2.3NH_4Cl$.	Found. I.	II.
Zn	22.00	22.02	21.80
Cl	59.76	60.13	59.47

Solutions of zinc chloride and ammonium chloride were made in the proportions of 1:1 and 1:4, in concentrated hydrochloric acid in order to see if the strong acid would cause the formation of salts different from those just described. The first crop of crystals from the 1:1 solution was the 1:3 salt of marignac, as was shown by their appearance and analysis. The other crops were composed of plates which proved to be the 1:2 salt. The 1:4 solution gave the 1:3 salt.

Dehérain says that when $ZnCl_2.NH_3$ and $ZnCl_2.4NH_3$ are dissolved in hydrochloric acid, corresponding double salts are formed. According to Kane,[1] $ZnCl_2.4NH_3.H_2O$ is formed when concentrated ammonia is added to a hot concentrated solution of zinc chloride, until the precipitate first formed is redissolved. On cooling, the salt is said to separate out in small brilliant plates with pearly luster. According to Marignac,[2] $ZnCl_2.2NH_3$ is often formed at once when the two solutions are brought together, as described by Kane. Kane says that, on further evaporation of the solution after removing the first crop of crystals, $ZnCl_2.2NH_3.\frac{1}{2}H_2O$ crystallizes out in radiating groups of square prisms of a brilliant vitreous luster. $ZnCl_2.NH_3$ is obtained, according to Kane, by heating $ZnCl_2.4NH_3.H_2O$ or $ZnCl_2.2NH_3.\frac{1}{2}H_2O$, ammonia and water being given off and a gummy mass remaining.

Following Kane's directions, as Dehérian also did, a compound was obtained, the analysis of which gave results agree-

1 Ann. chem. (Liebig) [2], **72**, 290. 2 Ann. des Mines [5], **12**, 1.

ing fairly well with the formula $ZnCl_2.4NH_3.H_2O$. The determination of zinc gave a figure which was less than the theoretical per cent. by 1.6 per cent. Some of the compound was dissolved in hydrochloric acid and allowed to crystallize. Small prismatic crystals were obtained that resembled, in all respects, the 1 : 3 salt described by Marignac. A determination of zinc was made, 0.2397 gram giving 0.0647 gram ZnO, *i. e.*, 21.74 per cent., the theoretical being 22.00 per cent. for the 1 : 3 salt.

On heating the rest of the compound, $ZnCl_2.4NH_3H_2O$, ammonia was given off and a gummy mass was left, as described by Kane. This was dissolved in hydrochloric acid and allowed to crystallize. Thin, shining plates were formed looking exactly like the 1 : 2 salt already described. It seems then, that dissolving these compounds in hydrochloric acid is equivalent to making solutions of zinc chloride and ammonium chloride in the proportions of 1 : 4 and 1 : 1, and we have seen that the former solution yields a 1 : 3 salt, while the latter yields a 1 : 2 salt.

In conclusion it may be said that all the salts described in this paper come under the law of double halides or the extension of the law.

$ZnCl_2.3C_6H_5NH_3Cl.2H_2O$,

m-$ZnCl_2.3C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown NH_3Cl \end{matrix}$,

p-$ZnCl_2.3C_6H_5 \begin{matrix} \diagup CH_3 \\ \diagdown NH_3Cl \end{matrix}$,

m-$ZnBr_2.3C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown NH_3Br \end{matrix}$,

$ZnCl_2.3NH_4Cl$,

are the salts that fall under the extension.

Biographical.

The author of this dissertation was born in Baltimore, Md., September 6, 1869. After attending the public schools he entered the Baltimore City College, from which he graduated in 1888. In the same year he entered the Johns Hopkins University, graduating as A.B. in 1891. Since then he has been pursuing a post-graduate course in chemistry, physics, and mathematics.